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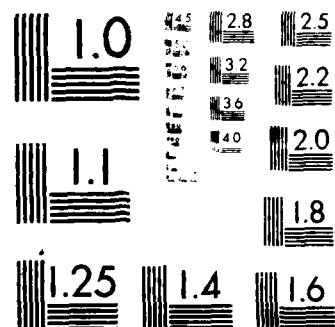
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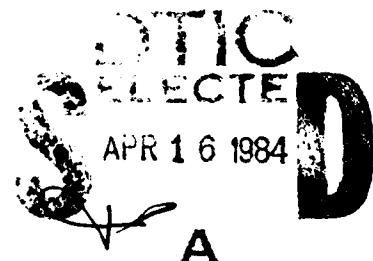
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DEVELOPMENT OF BIODEGRADABLE IMPLANTS
FOR USE IN MAXILLOFACIAL SURGERY

Annual Report

US ARMY INSTITUTE OF DENTAL RESEARCH
US Army Medical Research and Development Command

Project 4150-XIV



SOUTHERN RESEARCH INSTITUTE

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DEVELOPMENT OF BIODEGRADABLE IMPLANTS
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ANNUAL REPORT

Danny H. Lewis, Richard L. Dunn, Robert A. Casper

JUNE 1982

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I. SUMMARY

This report covers work performed during the first three quarters of the fourth contract year on Project 4150, Contract DAMD17-78-8059, "Development of Biodegradable Implants for Use in Maxillofacial Surgery." The report does not represent a final documentation of work conducted during the entire contract year and is intended rather to provide the US Army Institute of Dental Research (AIDR) with an update of the status of current project efforts only.

The objective of the project is to develop high-strength, bioabsorbable materials useful in the treatment and management of maxillofacial injuries. The specific goal for the current contract year has been the attainment of high-strength, high-modulus, biodegradable ceramic fibers for use in the reinforcement of biodegradable polymeric fracture-fixation plates. To meet this goal, we have examined the spinnability and processibility of β -tricalcium phosphate (whitlockite) and phosphate-free calcium aluminate. In studies conducted during the previous 2 years, composites fabricated from poly(DL-lactide)(DL-PLA) and commercially available, nonbiodegradable ceramic fibers were shown to provide sufficient strength and rigidity for use in the repair of mandibular fractures in dogs. Our work during the current renewal period has therefore been directed toward obtaining biodegradable ceramic fibers with mechanical properties sufficient for the fabrication of a totally biodegradable fracture-fixation appliance. *Z*

Initial studies determined the proper firing conditions for obtaining hard, dense ceramic test samples from pure, packed powders of whitlockite and phosphate-free calcium aluminate. Subsequent studies were directed toward screening a number of polymeric materials to determine their suitability for use as binding agents to aid in the fabrication, extrusion, and firing of the biodegradable ceramics. Barex 210, a terpolymer of acrylonitrile, butadiene, and methyl acrylate (available from Pfaltz and Bauer, Inc., Stamford, CT) was found to be the most thermally stable of the candidates examined.

Both wet- and dry-spinning processes were examined for producing continuous ceramic filaments. All dry-spinning efforts were unsuccessful. Wet-spinning using a spinning dope composed of the ceramic material, Barex 210, and solvent was more encouraging; continuous filaments were obtained using this procedure. These fibers were more stable during firing than materials prepared by other methods; however, fibers have yet to be obtained that approach the strength and ease of handling of commercial, nonbiodegradable ceramic fibers. Optimization studies concentrating on the effects of ceramic particle size and total ceramic loading will be required to obtain continuous, biodegradable ceramic fibers with properties sufficient for use in fabricating a totally biodegradable fracture-fixation appliance.



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II. INTRODUCTION

The need for improved methods and materials for the management of severe maxillofacial wounds is well recognized in view of the substantial portion of these received by soldiers in recent conflicts. In its investigations of various approaches to improved surgical methods and patient care, AIDR has constantly sought better materials for use in the repair of jaw fractures.

Bone consists of a framework of collagenous fibers, a mineral matrix, which is primarily calcium hydroxylapatite, and a small amount of the polysaccharides. Even though a large portion of the volume of bone is water, bones are hard and tough. Although varying considerably in properties depending on function, bones commonly have tensile strengths of 6000 to 20,000 psi and values of modulus of elasticity of 1 to 3×10^6 psi. Metals are stronger and stiffer than bone. Most polymeric materials are as strong as bone but more deformable and require fiber reinforcement or crosslinking to equal the stiffness of bone.

Fracture fixation in maxillofacial surgery has traditionally been accomplished by the use of rigid metallic fixation plates or cribs with metal bone screws used to attach the appliance to the surrounding bone. This method of fixation is less than satisfactory for two reasons: 1) rigid fixation devices, which are of primary importance in the promotion of initial fracture union, may cause cortical bone to atrophy as the healing process progresses and 2) additional surgical procedures are required for removal after healing is complete, thus increasing surgical cost and patient inconvenience.

Ideally, fixation appliances should vary in stiffness as healing progresses, transferring an increasing proportion of the mastication forces to the mandibular bone as it becomes further ossified. This progressive load transfer ensures that the forming bone is strained and exercised. Both processes are necessary for the formation of healthy hard tissue that has properties commensurate with those of virgin bone. The development of a variable-stiffness fixation device is best achieved by using a degradable polymer system with degradation products that are nontoxic and harmless to the host. A biodegradable material with properly tailored physical properties and degradation kinetics would ensure the development of strong, healthy bone and would eliminate the need for surgical removal of the fixation device on completion of the healing process.

Previous work has shown that composite materials with sufficient strength and rigidity for use in the treatment and management of mandibular fractures may be obtained by incorporating oriented, continuous, commercially available ceramic fibers into plates composed of DL-PLA. These fibers, however, are not biodegradable. Our efforts for the last three project quarters have been directed toward the development of continuous, biodegradable ceramic fibers for use in the reinforcement of DL-PLA plates to obtain a totally biodegradable fracture-fixation system.

III. PREPARATION OF BIODEGRADABLE CERAMIC FIBERS

Initially, we examined the fabrication and firing characteristics of β -tricalcium phosphate (whitlockite) with and without polymeric binders. We found that, in general, the dried, filtered green cake fired to a more acceptable product than either dried, ground green cake or dried, ground green cake with polymeric binders incorporated. We attributed the successful firing of dried, filtered whitlockite green cake to two factors. First, the green cake is produced by filtering and drying freshly precipitated tricalcium phosphate and, as such, is composed of particles of much finer size than would be the case for a material that has been dried and reground. Second, the lack of binder allows for a much closer packing density in the prefired state, resulting in greater densification during the sintering process than would be achieved with a material containing binder. We examined both dry- and wet-spinning processes for the production of ceramic fibers and, simultaneously, began an investigation of the methods available for reducing the particle size of ceramic materials to a level acceptable for successfully spinning fine fibers. We also examined phosphate-free calcium aluminate, another biodegradable ceramic, as an alternative to whitlockite. Preliminary wet-spinning results with both materials, using an acrylonitrile-based terpolymer as a binder, have been encouraging. Further optimization of particle size and binder content should lead to the successful production of biodegradable ceramic fibers for use in totally absorbable fracture-fixation appliances.

A. Fabrication and Firing of β -Tricalcium Phosphate (Whitlockite) Samples

At the initiation of the project, we attempted to determine a firing schedule suitable for producing hard, dense whitlockite ceramics. Initially, we used coarsely ground, dried green cake material for these studies, and we attempted to produce good-quality ceramics in both rod and plate form. For the preparation of rod specimens we packed a 0.062-in.-ID 8-in.-long alumina tube with dried green cake powder using a wooden dowel. A 0.75-in.-ID cylindrical alumina crucible was also packed with green cake powder in the same fashion. For preparation of ceramic plates, we used a 60 by 145-mm rectangular die. One plate was prepared using hand pressure. Another plate was prepared by compacting the green cake powder into the mold for 2 min under a pressure of 30,000 psi with a hydraulic press. All samples were placed in an oven at room temperature. The temperature was then raised to 2100 °F over a 3-h period, and the samples were sintered isothermally at this temperature for 1 h. The oven temperature was then reduced to 1650 °F and held at that point overnight. Then the heat to the oven was cut off, and the samples were allowed to cool slowly in the oven. Although neither of the rod specimens sintered to an intact material, both plates remained intact during the firing process. They were not very hard, however, and broke easily by hand.

We subsequently experimented with other pressure conditions for fabricating ceramic plates. Sturdy plates were obtained by maintaining a packing pressure of 40,000 psi for 1 min. Plates prepared in this fashion were less subject to cracking on transferral to alumina sintering trays than were plates prepared at other packing pressures. The plates were isothermally sintered for 1 h at 2100 °F, and the temperature was reduced to 1650 °F and held for 2 h. The oven was then turned off, and the plates were allowed to cool slowly to room temperature. The plates were hard, but could be broken by hand. In addition, the edges of the sintered plates were curled. We attempted to alleviate the curling problem by placing a ceramic brick on top of other plates that we prepared in a similar manner, but these plates curled during sintering as well.

We felt that better results could possibly be obtained through a judicious choice of particle size combinations. A sample of dried green cake was sieved on a mechanical shaker, and the variously sized fractions were collected and weighed. The particle size range distribution of a typical green cake material is presented in the tabulation below. Particles ranging from 150 to 250 μm accounted for the greatest portion of the distribution (27.7%); particles greater than 297 μm accounted for the smallest portion of the distribution (5.5%).

Particle size range, μm	Percentage of total wt
<53	23.8
53-106	21.8
106-150	11.6
150-250	27.7
250-297	9.6
>297	5.5

We packed cylindrical alumina crucibles with β -whitlockite particles of less than 53 μm . Packing was accomplished under hand pressure. The samples were placed in the oven at room temperature, heated to 2100 °F over a 3-h period, and sintered isothermally at this temperature for 1 h. The samples were then heat soaked at 1650 °F for 4 h and allowed to cool slowly to room temperature. The samples underwent volume reductions of 10 to 20%, and they were soft and sandlike.

We also fired samples composed of 30% (by weight) of particles less than 53 μm and 70% (by weight) of particles greater than 297 μm in the same fashion. There was little shrinkage in these samples, but they were soft and granular after firing.

Next, we investigated the effect of grinding on the sintering characteristics of dried, filtered green cake. A dried green cake sample was prepared,

and a section of the green cake was removed and ground. The unground material was further dried in an oven at 120 °C for 50 h; the ground material was dried at 90 °C for 17 h. Both samples were sintered isothermally at 2100 °F for 5 h. The oven was then turned off, and the samples were allowed to cool slowly to room temperature. The ground specimen was soft and sandlike after sintering. The unground specimen, however, was quite hard and had a smooth texture. Subsequent analysis by scanning electron microscopy (SEM) showed the unground specimen to have a high packing density with few void spaces. Sintering of another unground sample at 2100 °F for 1 h, with a subsequent 4-h soak at 1650 °F, gave similar results.

B. Effect of Various Binders and Coatings on the Sintering Characteristics of Whitlockite

Filtered, unground, dried whitlockite green cake produced hard, dense ceramics on firing. Unfortunately, such a material does not lend itself to extrusion into the fibers desired for bone-plate reinforcement. Binding agents have been used for many years to facilitate the extrusion and molding of ceramic materials, and thus, we investigated a number of polymeric materials as binding and plasticizing agents for the extrusion of whitlockite rods and fibers. As a preliminary step to fiber-production studies, we examined the influence of these various agents on the sintering process of whitlockite.

We initially investigated hydroxyethylcellulose (HEC) as a binding material. The HEC, as a 2% solution in water, was combined with green cake at various stages of dryness to produce smooth pastes. The pastes were then injected, individually, into 0.1875-in.-ID hollow alumina rods. Replicate samples, without binder, were fabricated similarly. All samples were dried for 16 h at 90 °C, and they were then sintered isothermally at 2100 °F for 1 h and heat soaked at 1650 °F for 4 h. The oven was turned off, and the samples were allowed to cool slowly to room temperature.

All samples cracked after drying at 90 °C. No additional cracking was observed during the sintering process, and each of the samples sintered to a hard, crystalline form. When tested, the samples broke along crack lines propagated during the drying process. We also noted that greater shrinkage occurred in the formulations containing HEC.

We subsequently examined a procedure in which we mixed the aqueous HEC solution with re-suspended green cake material (50%, v/v). The resulting thick white mixture was filtered with a Buchner funnel until a pastelike filtrate was obtained. The paste was then extruded into 0.0625-in.-diameter rods using a disposable, plastic syringe. These rods appeared to be smoother and to contain fewer breaks than rods extruded from filtrate containing no binder. Some of the samples were dried in a 90 °C oven; other samples were air dried overnight. The samples dried at 90 °C fractured and curled, while the air-dried samples curled, but did not fracture. The samples were sintered according to the firing schedule given previously for samples containing HEC. There was no further cracking during the sintering process, and although the samples could be broken by hand pressure, they exhibited a sharp snap during breakage, indicating a hard, brittle product.

Poly(vinyl alcohol) (PVA) and poly(ethylene oxide) (PEO) were also investigated as binders. Filtered, unground green cake was mixed with a small quantity of 10% PVA in water to obtain a smooth paste. Small rodlets of this material were obtained by extruding the paste with a disposable plastic syringe. Rodlets were also prepared from a paste made from filtered, unground green cake and 10% PEO. Rodlets consisting of filtered, unground green cake containing no binder were used as controls. The rodlets were air dried for 3 h and oven dried for 18 h at 90 °C. All samples were sintered isothermally at 2100 °F for 1 h and were heat soaked at 1650 °F for 4 h following sintering. The oven was then turned off, and the samples were allowed to cool slowly to room temperature. All samples cracked after drying at 90 °C. No additional cracking was observed during sintering, but each of the samples sintered to a brittle form.

We also examined lanolin, glycerol, silicone oil, and polycaprolactone (PCL) as potential binding agents. Rods fabricated using lanolin, glycerol, and silicone oil as binding agents did not hold together during drying, so these samples were not sintered. Tough elastic rods were prepared by mixing dried green cake with molten PCL and extruding through a 0.05-in.-diameter spinneret using a bench-scale melt indexer at 90 °C. The rods were dried for 16 h at 90 °C, sintered at 2100 °F for 1 h, heat soaked at 1650 °F for 4 h, and then allowed to cool slowly to room temperature. The rods did not sinter well, and they were broken and very fragile.

The use of binders did not, in any case, produce products of acceptable quality after sintering. Because migration of binding agents may have been responsible for crack introduction and propagation as well, we examined a number of materials as coatings for extruded whitlockite materials.

Whitlockite green cake was filtered almost to dryness using a Buchner funnel. The filter cake was then removed and extruded into rodlets using a disposable, plastic syringe. The rodlets were separated and coated with the following formulations: 2% HEC in water, 12% Estane in tetrahydrofuran (THF), and 13% poly(DL-lactic acid) (DL-PLA) in dioxane. Rodlets coated with each of the formulations broke up severely on drying, both at room temperature and at 90 °C.

C. Dry-Spinning Trials on Whitlockite

Although we were unsuccessful in producing samples with good sintering characteristics using the syringe or melt-index method, we felt that more acceptable materials might be produced using a ram extruder capable of generating high, more uniform extrusion pressures. Thus, we conducted dry-spinning trials on whitlockite with and without binder under these conditions. The ram extruder was equipped with an electrically heated metal spinning block 4 in. in diameter and 8 in. in length with a 0.6-in. diameter bore through the center. The bore was 7 in. long. The extruder was driven by a 0.6-in.-diameter ram driver equipped with a variable-speed motor. A pressure gauge was located directly above the ram to measure the force applied to the ram. A surface-driven winder was located about 3 ft below the spinneret for collecting spun fiber on paper tubes. The spinneret

used in these trials had a single 0.020-in.-diameter orifice 0.040 in. in length. The filter screen consisted of a single 40-mesh stainless steel screen.

For paste containing no binder, the paste was charged to the extruder at room temperature, and extrusion was attempted at a feed rate of about $1.35 \text{ cm}^3/\text{min}$. We were unable to extrude filaments continuously. Some short lengths of the monofilament were extruded and collected by hand before the paste became too viscous to flow, but these monofilaments were too weak to support their own weight. The filaments dried rapidly at ambient conditions and shrank so rapidly that they broke into several pieces. The dried filaments were brittle and fractured too badly for sintering.

We also attempted to extrude whitlockite paste containing PEO. An aqueous solution of PEO (1%) was added to whitlockite powder until a thick paste was obtained. The particle size of the powder was $< 150 \mu\text{m}$. We deaerated the paste in a vacuum desiccator prior to extrusion. Extrusion was attempted using the same extruder and spinneret described previously, but no filament flow occurred. Some water extruded as the pressure ($\approx 3500 \text{ psi}$) was applied to the paste, and the paste formed a hard cake. The trial was repeated with another sample of the same paste, but the ram block was heated to 105°C . Again, no filament flow was obtained. Dry-spinning of both pastes and pastes containing binder were unsuccessful in producing an acceptable fiber from whitlockite.

D. Evaluation of Phosphate-Free Calcium Aluminate

Because dry-spinning of whitlockite had proven unsuccessful, we began to examine phosphate-free calcium aluminate as an alternative to whitlockite. Phosphate-free calcium aluminate is both bioabsorbable and biocompatible. As such, it provides an alternative to hydroxyapatite materials for use as a reinforcement for biodegradable fracture-fixation plates. Therefore, we examined the dry-spinning and sintering characteristics of pastes made from phosphate-free calcium aluminate and PEO as well as the sintering characteristics of pressed calcium aluminate powders containing no binder.

Phosphate-free calcium aluminate was obtained from the Research Division of Pfaltz and Bauer, Inc., Stamford, CT. The powder, as supplied, was less than 200 mesh. Initially, we investigated the sintering characteristics of packed, dry powder. Calcium aluminate powder was placed in a Mylar-lined, 2-in.-diameter steel die. The sample was then pressed at 10,000 psi for 2 min using a hydraulic press. The pressed sample was then placed in an oven heated to 800°F . The oven temperature was raised to 1650°F over a 1-h period. The sample was maintained at this temperature for 22 h and then removed from the oven and allowed to cool to room temperature. The resulting material was soft and flaky.

Subsequently, a duplicate sample was placed in an oven heated to 1650°F . The oven temperature was increased to 2100°F over a 2-h period, and the sample was maintained at this temperature for 18 h. The sample was then removed from the oven and allowed to cool to room temperature. This sample was harder than the sample subjected to the firing schedule described previously.

Next, we examined the sintering characteristics of phosphate-free calcium aluminate containing PEO as a binder material. A 10% (w/w) PEG/water solution was prepared using 300,000 molecular weight PEO. Calcium aluminate, 10 g, was ground with a mortar and pestle and mixed with 3 g of the 10% PEG/water solution until a thick, gray paste was obtained. The paste was hand-molded into a rectangular cube and placed in an oven maintained at 1650 °F for 15 h. The oven temperature was increased to 2100 °F, and the sample was maintained at this temperature for an additional 15 h. The sample was then removed from the oven and allowed to cool to room temperature. The resulting material was light and hard, exhibiting little chipping. Samples containing higher concentrations of binder and subjected to the same firing conditions were more fragile than samples containing less binder.

We also examined the possibility of extruding phosphate-free calcium aluminate paste into fiber form by a dry-spinning process. A paste of phosphate-free calcium aluminate was prepared by mixing 10 g of phosphate-free calcium aluminate with 3 g of 10% PEO/water solution. The paste was loaded into the chamber of a melt extruder and extruded through a 0.05-in.-diameter spinneret using a 17-kg mass. We were able to extrude continuous rods at room temperature by this process. The rods were allowed to dry at room temperature for 2.5 h and then placed in a 2100 °F oven for 18 h. After firing, some of the rods were removed from the oven and quickly cooled to room temperature. Another batch of extruded rods was allowed to cool slowly to room temperature inside the oven. Rods subjected to both cooling cycles were smooth and exhibited crack-free surfaces. Both sets of rods, however, were granular in cross section and could be reduced to a powder by hand pressure.

E. Preparation of Fine-Grained (<10 µm) Whitlockite Particles by Microencapsulation

Because dry-spinning of both whitlockite and phosphate-free calcium aluminate had proven unsuccessful, we turned our attention to the production of fine-grained whitlockite in an attempt to obtain better extrusion characteristics and greater densification on firing.

Abrasive grinding of ceramic materials, such as that encountered in ball milling, is plagued by excessive time requirements and low yield of small-particle-size fractions. We have been successful in preparing small-diameter polymeric spheres by microencapsulation techniques in a number of our other research projects, and we investigated microencapsulation as a means of producing hydroxyapatite particles of a size sufficient for producing fine fibers. We attempted to prepare microspheres of hydroxyapatite by the process described below.

An aqueous solution of calcium nitrate $[\text{Ca}(\text{NO}_3)_2]$ was prepared by combining calcium nitrate (330.6 g; 1.40 mol) with 800 mL of deionized water in a 3-L beaker equipped with a stir bar. The solution was continuously stirred as the calcium nitrate was added. The pH of the solution was adjusted to 11.1 by the addition of ammonium hydroxide (NH_4OH). The solution was then diluted to 1800 mL with deionized water. Next, a solution of dibasic ammonium phosphate $[(\text{NH}_4)_2\text{HPO}_4]$ was prepared by combining dibasic

ammonium phosphate (132 g; 1.00 mol) with 1500 mL of deionized water. The pH was then adjusted to 11.1, and a white precipitate formed. The solution was diluted to 3800 mL with deionized water, and the precipitate dissolved. The final solution pH was determined to be 10.9.

Next, 400 mL of Dow 200 Silicone Fluid was added to a 1-L resin kettle equipped with a 2.5-in. Teflon turbine impeller powered by a G-K Heller stir motor. Stirring (4000 rpm) of the silicone fluid was initiated, and the calcium nitrate solution was added to form a water-in-oil emulsion. Dibasic ammonium phosphate solution was slowly added (4 mL/min) to the emulsion with continuous stirring. Stirring was continued for 30 min to allow the product to precipitate into the aqueous phase. A vacuum (1.8 psi) was then pulled on the system, and the solution was heated to remove water. After water removal was complete, the kettle contents were poured into 3-L of heptane, and the microspheres were allowed to settle out overnight. Subsequently, the excess heptane was decanted, and the product was placed in a vacuum oven to remove the residual heptane. Microscopic examination showed discrete microspheres of small diameter. On drying, the spheres coagulated to form a continuous film.

Although the microencapsulation procedure demonstrated the feasibility of producing small-particle-size hydroxyapatite, we were unable to maintain particle integrity during the drying process. This is clearly demonstrated in the photomicrograph by scanning electron microscopy (SEM) shown in Figure 1. In an effort to maintain particle integrity, we encapsulated microspheres of hydroxyapatite in ethyl cellulose by the following procedure: Dow Corning 200 Silicone Fluid, 400 mL, was added to a 1-L resin kettle. An oil-in-water emulsion was formed by adding 50 mL of calcium nitrate solution to the silicone oil, as described in the previous preparation. Next, 89 mL of dibasic ammonium phosphate solution was added to the emulsion at a rate of 5 mL/min. Resin kettle contents were stirred at 4000 rpm during both calcium nitrate and ammonium phosphate addition. Stirring was continued for 30 min after the ammonium phosphate addition was complete. Vacuum was then applied to the system, and the kettle was heated to 100 °C for 2.5 h to remove the water.

Next, the contents of the resin kettle were poured into a large flask containing 2.5 L of ethyl acetate, and the contents were stirred for 15 min to wash the silicone oil from the hydroxyapatite particles. Stirring was then stopped, and the large particles were allowed to settle. The supernatant was decanted and centrifuged at 4000 rpm for 20 min. The settled particles were then collected and resuspended in 100 mL of ethyl acetate.

Next, 1.0 g of ethyl cellulose was added to the 100 mL of ethyl acetate containing the hydroxyapatite particles. The ethyl cellulose was phase separated around the hydroxyapatite particles by adding 15 mL of silicone oil to the solution at a rate of 4 mL/min. The solution was then added to a resin kettle containing 2 L of heptane and stirred for 10 min. Next, the kettle contents were poured into two 1-L centrifuge bottles and centrifuged at 4000 rpm for 10 min. The excess heptane was then decanted, and the ethyl cellulose-coated hydroxyapatite particles were placed in a vacuum oven to dry.



Figure 1. Non-coated hydroxyapatite particles after drying.

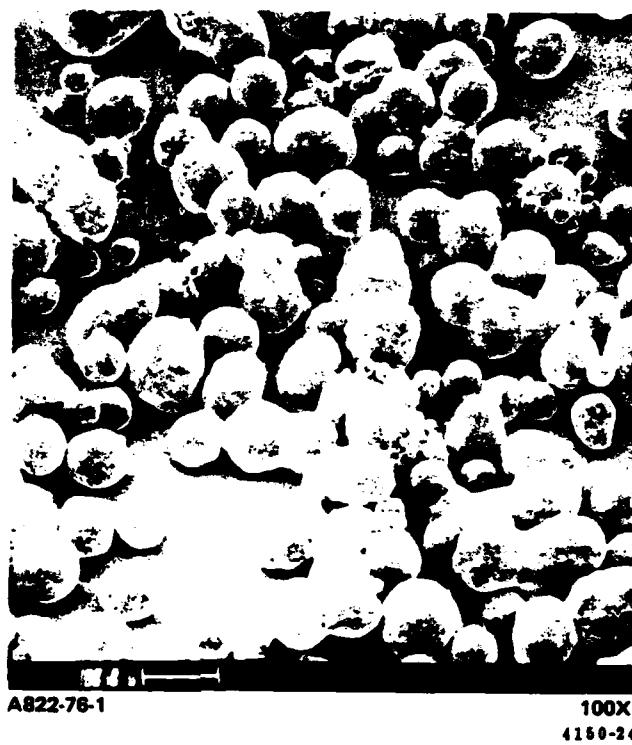


Figure 2. Hydroxyapatite particles coated with ethyl cellulose.

The photomicrograph presented in Figure 2 shows that we were able to obtain microspheres of hydroxyapatite coated with ethyl cellulose in the 40- to 50- μm range by this procedure. We extruded the coated particles into a 0.05-in.-diameter rod with a melt indexer operating at 180 °C. The rod was placed in an oven heated to 2150 °F and maintained at this temperature for 4 h. The oven was then turned off and allowed to cool slowly to room temperature. The rod did not sinter and was highly fragmented. At this time, although microencapsulation has been shown to produce small particles, the necessity of coating the particles to prevent agglomeration during drying would seem to preclude fiber formation with particles prepared by this procedure because the polymers used for coating do not have sufficient thermal stability to bind the spheres together until sintering has been initiated.

F. Preparation of Ceramic Fibers by Wet-Spinning

As an alternative to dry spinning, we examined the possibility of using wet spinning to produce fibers from both whitlockite and phosphate-free calcium aluminate. The process involves extruding a ceramic/binder/solvent mixture into a coagulation bath. Fibers are drawn from the coagulating bath through a rinsing and drying system to remove the solvent and are then taken up on a winding reel. After soaking in water to remove the remaining solvent, the fibers are air dried and finally oven sintered. Following is a detailed description of the ceramic fiber spinning process for both types of ceramic.

Hydroxyapatite and calcium aluminate $[\text{Ca}(\text{AlO}_2)_2]$, from Pfaltz and Bauer, Inc.] are powders of about 200 mesh. The calcium aluminate was sieved to obtain particles $<50\ \mu\text{m}$ in size to aid in mixing the dispersion and to produce greater densification during the firing process. The spinning process was similar for both types of powdered ceramics. Both powders were mixed with a binder/solvent solution of Barex 210, a terpolymer of acrylonitrile, butadiene, and methylacrylate, in N,N -dimethylacetamide at a weight percentage ratio of 25:75 (Barex 210/solvent). The ceramic powders were dispersed in the binder solution by slow addition of the powders to well-stirred binder solutions. Spinning dopes containing 40% hydroxyapatite and 60% Barex 210 and 70% phosphate-free calcium aluminate and 30% Barex 210 were prepared in this manner.

For spinning trials on each material, the spinning dope was loaded into a cylindrical, stainless steel feed pot. The feed pot was pressurized with compressed air (20 psi), and the spinning dope was forced from the feed pot through stainless steel tubing (0.25-in.-OD, type 304) to a Zenith gear pump driven by a Zenith Model QM drive motor. The Zenith pump delivered the spinning dope (at $0.29\ \text{cm}^3$ per revolution) to a spinneret with an orifice diameter of 0.020 in. The spinneret was submerged in a water bath. As the spinning dope came in contact with the water, it coagulated to form a fiber. After traversing the coagulation bath (18 in.), the fiber was taken up by the first godet. This godet was heated and equipped with a tap water spray to remove solvent from the fiber. The fiber was then taken up on a second heated godet and rinsed with a warm water spray. The fiber was passed around a third heated godet and collected on a Leesona Model 955 take-up winder.

The spinning conditions for the hydroxyapatite material were as follows:

Spinning dope: 10% β -whitlockite
 15% Barex 210
 75% N,N-dimethylacetamide

Pump rate of dope: 1.45 cm³/min

Coagulating bath: tap water at 70 °F

Godet No.	Surface speed, ft/min	Godet temp., °F
1	80	107
2	84	97
3	87	105

Conditions for spinning calcium aluminate fibers were as follows:

Spinning dope*: 70% phosphate-free calcium aluminate
 30% Barex 210

Pump rate of dope: 1.75 cm³/min

Coagulating bath: tap water at 70 °F

Godet No.	Surface speed, ft/min	Godet temp., °F
1	94	110
2	94	115
3	96	115

The hydroxyapatite fibers were white and more elastic than the calcium aluminate fibers because of a higher binder content. The calcium aluminate fibers were gray initially, but turned dull-white during final drying. The calcium aluminate fibers were more brittle than the hydroxyapatite fibers because of a higher solids loading. The fibers were soaked in deionized water for 3 days to remove the remaining solvent. After soaking, the fibers were air dried prior to firing.

The sintering furnace consisted of an 8-in.-diameter heater cavity surrounded by a water-cooled furnace shell. It was equipped with a water-cooled copper electrode, a site port, and an alternating-current power supply. A powerstat (0 to 270 V, 0 to 200 amps) was used to control power to the power transformer (0 to 50 V, 0 to 2000 amps). The furnace was purged with nitrogen gas through the heater cavity, the site port, and the furnace shell.

*Formulation refers to product after solvent removal.

Fiber samples were placed on Grafoil trays for firing. The trays were stacked one on top of the other to allow nitrogen gas to circulate around all fibers.

The samples were placed in the furnace at room temperature, and the temperature was increased linearly over 5 h to 2150 °F. The samples were maintained at this temperature for 1 h. The oven temperature was then decreased to 1650 °F over a 2-h period, and the samples were soaked at 1650 °F for 4 h. The furnace was then turned off, and the fibers were allowed to cool slowly in the furnace.

The hydroxyapatite fibers were shiny, black, and fragmented. This condition was a result of high binder content and large particle size. The calcium aluminate fibers were intact and white. Both types of fibers were brittle, but the phosphate-free calcium aluminate fibers were more satisfactory than were the hydroxyapatite fibers.

At present, we are waiting for the return of ceramic samples that have been sent outside the Institute for particle-size reduction. Wet-spinning trials will be resumed on both whitlockite and phosphate-free calcium aluminate as soon as the samples arrive. With ceramic powders of finer (<10- μ m) particle size and higher solids loadings, we should be able to produce the high-strength, small-diameter fibers required for fixation-plate reinforcement.

IV. CONCLUSIONS AND RECOMMENDATIONS

During the last 3 years, we have shown that DL-PLA plates reinforced with commercially available nonbiodegradable ceramic fibers were of sufficient strength and rigidity to be used in the treatment and management of mandibular fractures. During the course of the last year, our specific goal has been to produce a biodegradable ceramic fiber (whitlockite or phosphate-free calcium aluminate) for use in plate reinforcement to yield a totally biodegradable fixation appliance. As yet, we have been unsuccessful in producing a continuous fiber with the desired properties. Firing schedules for producing good-quality ceramics of both materials were investigated, and hard, dense ceramics were produced from whitlockite. It is our opinion that the production of a high-quality ceramic from dried, unground whitlockite green cake was a result of both finer particle size and increased packing density.

We feel that particle size distribution and packing density, in conjunction with the examination of other polymeric binding systems and firing atmospheres, must be further investigated to optimize the present ceramic systems. With further effort in these areas, we feel that we will be able to produce continuous, biodegradable ceramic fibers with the properties required for DL-PLA plate reinforcement.

V. ACKNOWLEDGMENTS

Mr. James A. Ryan, Jr., Assistant Chemist, and Mr. James P. English, Research Chemist, have been instrumental in carrying out various phases of the experimental work. Mr. English has also made valuable suggestions in the preparation of fibers by the wet-spinning process.

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